Nighttime Lagrangian Measurements of Aerosols and Oxidants:
Homogeneous and Heterogeneous Chemical Processing of NO$_x$

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1. INTRODUCTION

Although heterogeneous chemical processes involving trace gases and aerosols are poorly understood they are expected to play an important role at night. ASP's 2002 Nighttime Aerosol Oxidant Plume Experiment (NAOPEX) was designed to study the chemical evolution and interaction of ambient aerosols and trace gases in the absence of photochemistry. Quasi-Lagrangian measurements were made with DOE's G1 aircraft in the nocturnal residual layer downwind of Boston, MA.
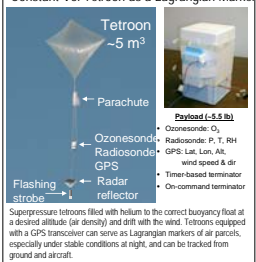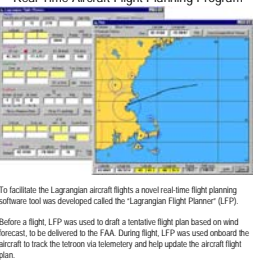
2. G1 AIRCRAFT MEASUREMENTS

Measurement	Instrument	Groups
Aerosol Size Distribution	FSSP, PCASP, CPC, TSEMS	PNNL, Brechtel
Aerosol Composition	AMS, PILS, Single Particle Analyzer	Aerodyne, BNL, PNNL
Aerosol Optical Properties	Integrating Nephelometer, Radiance PSAP	PNNL
Inorganic Gases	O$_3$, CO, SO$_2$, NO, NO$_2$, NO$_y$	PNNL & BNL
VOC	Canister sampling system	York Univ.
Meteorology	T, P, Dew Pt, Vector Winds (Gust Probe)	PNNL

3. LAGRANGIAN FLIGHT PLANNING TOOLS

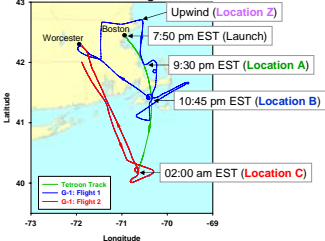Constant-Vol Tetroon as a Lagrangian Marker

Tetroon ~5 m^3

Parachute

Ozonesonde Radiosonde GPS

Flashing strobe

Radar reflector

Payload (~5.5 lb)
- Ozonesonde: O$_3$
- Radiosonde: P, T, RH
- GPS: Lat, Lon, Alt, wind speed & dir
- Timer-based terminator
- On-command terminator

Superpressure tetroons filled with helium to the correct buoyancy float at a desired altitude (air density) and drift with the wind. Tetroons equipped with a GPS transceiver can serve as Lagrangian markers of air parcels, especially under stable conditions at night, and can be tracked from ground and aircraft.

Real-Time Aircraft Flight Planning Program

To facilitate the Lagrangian aircraft flights a novel real-time flight planning software tool was developed called the 'Lagrangian Flight Planner' (LFP).

Before a flight, LFP was used to draft a tentative flight plan based on wind forecast, to be delivered to the FAA. During flight, LFP was used onboard the aircraft to track the tetroon via telemetry and help update the aircraft flight plan.

4. JULY 30-31 EPISODE

G1 and Tetroon Flight Tracks

Upwind (Location Z)
7:50 pm EST (Launch)
9:30 pm EST (Location A)
10:45 pm EST (Location B)
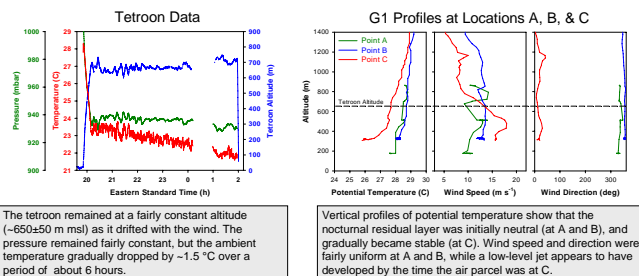02:00 am EST (Location C)

Lagrangian measurements were made within a column of air, which passed over the Salem coal-fired power plant around 7:35 pm on July 30, and continued to move south through the night. (Sunset ~7:00 pm EST)
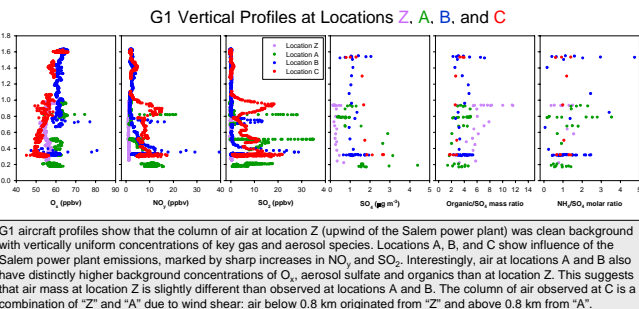
The G1 aircraft made four vertical profiles in the vicinity of the tetroon at different times, marked as locations Z, A, B, and C in the adjacent figure.

Time evolution of the meteorological variables and chemical species are described next.
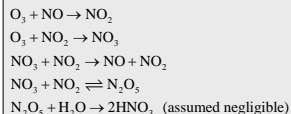
5. METEOROLOGICAL OBSERVATIONS

Tetroon Data

G1 Profiles at Locations A, B, & C

The tetroon remained at a fairly constant altitude (~650±50 m msl) as it drifted with the wind. The pressure remained fairly constant, but the ambient temperature gradually dropped by ~1.5 °C over a period of about 6 hours.

Vertical profiles of potential temperature show that the nocturnal residual layer was initially neutral (at A and B), and gradually became stable (at C). Wind speed and direction were fairly uniform at A and B, while a low-level jet appears to have developed by the time the air parcel was at C.

6. QUASI-LAGRANGIAN GAS-AEROSOL OBSERVATIONS

G1 Vertical Profiles at Locations Z, A, B, and C

G1 aircraft profiles show that the column of air at location Z (upwind of the Salem power plant) was clean background with vertically uniform concentrations of key gas and aerosol species. Locations A, B, and C show influence of the Salem power plant emissions, marked by sharp increases in NO$_y$ and SO$_2$. Interestingly, air at locations A and B also have distinctly higher background concentrations of O$_x$, aerosol sulfate and organics than at location Z. This suggests that air mass at location Z is slightly different than observed at locations A and B. The column of air observed at C is a combination of "Z" and "A" due to wind shear: air below 0.8 km originated from "Z" and above 0.8 km from "A".

7. MODEL ANALYSIS

Nighttime Chemical Processing of NO$_x$

Gas-phase Reactions

$$O_3 + NO \rightarrow NO_2$$
$$O_3 + NO_2 \rightarrow NO_3$$
$$NO_3 + NO_2 \rightarrow NO + NO_2$$
$$NO_3 + NO_2 \rightleftharpoons N_2O_5$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad \text{(assumed negligible)}$$

Heterogeneous Reactions

$$N_2O_5 + H_2O \xrightarrow{sfc} 2HNO_3 \quad (\gamma_{N_2O_5} = 0.001 - 0.02)$$
$$NO_3 \xrightarrow{sfc} NO \quad (\gamma_{NO_3} = ?)$$
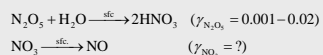
A detailed gas chemistry model is applied to simulate the chemical evolution within the tagged column of air since it passed over the Salem power plant up to locations A, B, and C.
**The objective is to examine the role and importance of the heterogeneous reaction of NO$_3$**

Initial Conditions and Model Constraints:
The model column points for each location are initialized and constrained as follows:
[O$_3$]$_0$ = 61 ppbv (corresponding to the uniform vertical O$_x$ profile at locations A and B)
[NO]$_0$ = observed NO$_y$ at that location
Aerosol Size Dist. = observed PCASP Aerosol Size Dist. at that location (particles greater than 0.11 μm only)
T, P, RH = observed T, P, RH at that location
Model integration time (Δt) = (time at that location) – (time when column was over Salem power plant)
(for location C, wind speed shear is taken into account when calculating Δt, and
[O$_3$]$_0$ = 55 ppbv below 0.8 km, corresponding to the uniform vertical O$_x$ profile at location Z).

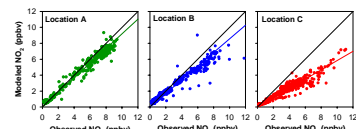The predicted O$_3$ and NO$_2$ are compared with the observed values at the respective locations.
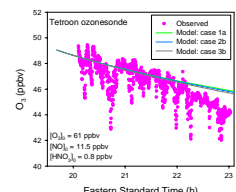
CASE 1a: $\gamma_{N_2O_5} = 0$, $\gamma_{NO_3} = 0$
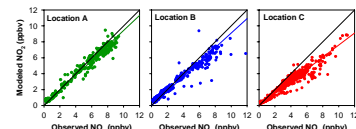
CASE 2a: $\gamma_{N_2O_5} = 0.001$, $\gamma_{NO_3} = 0$
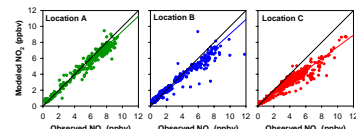
CASE 3a: $\gamma_{N_2O_5} = 0.02$, $\gamma_{NO_3} = 0$

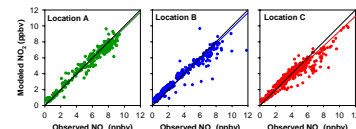Model systematically under-predicts NO2 as a function of processing time, especially at higher values of γ_{N2O5}. While the actual value of γ_{N2O5} cannot not be determined from this dataset, its value is thought to be between 0.001 to 0.02.

CASE 1b: $\gamma_{N_2O_5} = 0$, $\gamma_{NO_3} = 0.01$

CASE 2b: $\gamma_{N_2O_5} = 0.001$, $\gamma_{NO_3} = 0.01$

CASE 3b: $\gamma_{N_2O_5} = 0.02$, $\gamma_{NO_3} = 0.04$

Including heterogeneous conversion of NO$_3$ to NO can largely correct the discrepancy at all three locations. Depending on the choice of γ_{N2O5} the value of γ_{NO3} ranges between 0.01 to 0.04, representing the upper limit.
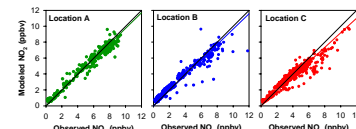

Modeled decay of O$_3$ agrees remarkably well with the Lagrangian measurement onboard the tetroon for the first two hours, but shows some deviation afterward.
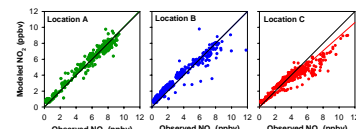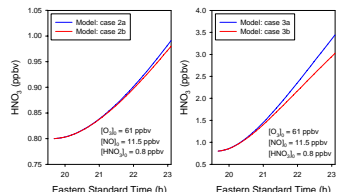

The heterogeneous NO$_3$ to NO reaction tends to slow down HNO$_3$ production, and could be important at higher values of γ_{NO3}.

7. CONCLUSIONS & CLOSING REMARKS

Model analysis of the quasi-Lagrangian aircraft dataset appears to provide indirect evidence of the heterogeneous conversion of NO$_3$ to NO (or possibly NO$_2$), with an uptake coefficient between 0.01 and 0.04. This represents an upper limit since the aerosol surface area is estimated using only particles greater than 0.11 μm diameter. Laboratory experiments are needed to study heterogeneous conversion of NO$_3$ on coal-fired power plant aerosols, which are composed of potentially reactive fly ash material.

8. ACKNOWLEDGEMENTS

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